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I, JANENE PEISKER, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2003906724 for a patent by UNISEARCH LIMITED as filed on 04 December 2003.

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Patents Act 1990

PROVISIONAL SPECIFICATION

Applicant:

UNISEARCH LIMITED

A.C.N. 000 263 025

Invention Title:

METHOD FOR DECONTAMINATING SURFACES

The invention is described in the following statement:

METHOD FOR DECONTAMINATING SURFACES

FIELD OF THE INVENTION

The present invention relates to a method for chemically altering contaminants on the surface of a solid substrate. The method may be used to decontaminate contaminated surfaces.

BACKGROUND ART

The surface of a solid substrate can become contaminated with various contaminants. The contaminants may be non-toxic substances such as dirt, or substances harmful to humans, animals or the environment, such as toxic industrial pollutants (e.g. halogenated organic compounds), pesticides, herbicides, or chemical or biological warfare agents.

The contamination of the surface may limit the uses that may be made of the substrate. A contaminated surface may be decontaminated by treating the surface to remove the contaminants from the surface, or by treating the surface to destroy the contaminants or to convert the contaminants to other substances that have lesser impact on the intended use of the substrate.

When the contaminant is a relatively harmless substance, the contaminant may be removed from the surface by washing the surface with a liquid such as water or an organic solvent to wash the contaminant from the surface. However, washing a surface simply removes the contaminant from the surface with the liquid, and for harmful contaminants, the liquid containing the contaminant may be difficult to dispose of safely or may itself need to be treated to remove the contaminant from the liquid. Further, washing the surface may not remove a sufficient amount of a harmful contaminant to render the surface harmless to humans, animals or the environment.

The main methods used to decontaminate surfaces contaminated with harmful substances such as toxic industrial pollutants, pesticides or chemical or biological warfare agents, are neutralisation which involves chemically altering the contaminant to form less harmful products, and absorption which physically removes the contaminant from the surface but does not result in its destruction (e.g. using Fullers earth or activated charcoal).

Neutralisation is a preferred method for decontaminating surfaces contaminated with

toxic substances as the method results in the destruction of the contaminant. For example, the most widely used method for neutralisation of chemical or biological warfare agents on a surface involves the use of hypochlorite to oxidise the contaminant into less harmful or harmless products. However, hypochlorite formulations have a number of disadvantages, including a reduction in active chlorine content over time and the corrosivity, flammability and toxicity of the formulation.

Zero valent iron (ZVI) has been used for degrading organic contaminants (including chlorinated and nitro-substituted organic compounds) in groundwater. This degradation process involves the oxidation of Fe^0 and the reduction of the organic contaminant. This degradation process is carried out under fully anoxic conditions since the presence of oxygen would prevent, or lower the efficiency of, the reduction of the contaminant.

A recent article has reported the oxidative destruction of chlorophenols in water in the presence of granular iron and EDTA, a strong iron binding ligand (Noradoun, C., et al (2003) "Destruction of Chlorinated Phenols by Dioxygen Activation under Aqueous Room Temperature and Pressure Conditions", Ind. Eng. Chem. Res., 42, 5024-5030). That article reported that no oxidative degradation of the chlorophenol in the presence of granular iron was observed (even after 70 hrs) in the absence of EDTA.

There remains a need for alternative methods for treating contaminated surfaces to remove the contaminant or chemically alter the contaminant.

It is to be understood that a reference herein to a prior art document does not constitute an admission that the document forms part of the common general knowledge in the art in Australia or in any other country.

SUMMARY OF THE INVENTION

The present inventors have surprisingly found that particles of zero valent iron or other metals can be applied, in the presence of air, to surfaces contaminated with various contaminants, to chemically modify the contaminants on the surface. The present inventors have found that when particles of zero valent iron or other metals are applied to a surface in the presence of air, the contaminants on the surface are primarily chemically altered by oxidation of the contaminant, rather than reduction of the contaminant as is the case in the prior art anoxic processes for degrading contaminants in groundwater using zero valent iron.

In a first aspect, the present invention provides a method for treating a surface of a solid substrate to chemically alter contaminants on the surface capable of being oxidised by hydroxyl radicals, said method comprising applying to the surface particles of a zero valent metal capable of reacting with oxygen and water to form hydroxyl radicals, and exposing the particles to oxygen and water to form hydroxyl radicals at or near the surface.

Typically, the zero valent metal particles are exposed to oxygen and water by exposing the particles to an atmosphere containing oxygen and water. Typically, the particles are applied to the surface and simultaneously exposed to oxygen and water, by applying the particles to the surface in the presence of an atmosphere containing oxygen and water vapour, typically air. Preferably, the zero valent metal particles are applied to the surface in admixture with water, or water is applied to the surface before, after or simultaneously with the application of the particles, so as to form a thin film of a mixture of water and the particles on the surface.

Typically, the zero valent metal is iron or copper, more typically iron. However, other zero valent metals capable of reacting with oxygen and water to form hydroxyl radicals could be used.

Typically, the particles of the zero valent metal are nano-sized particles of the metal.

In some embodiments, the nano-sized zero valent metal particles are applied to the surface as a powder. In other embodiments, the nano-sized zero valent metal particles are applied to the surface in admixture with a liquid carrier, typically water.

In a second aspect, the present invention provides zero valent metal particles when used in the method of the first aspect of the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The method of the present invention comprises applying particles of a zero valent metal to the surface, and exposing the particles to oxygen and water to form hydroxy radicals at or near the surface.

Typically, the particles of the zero valent metal are exposed to oxygen and water by exposing the particles to an atmosphere containing oxygen and water, such as air. Typically the particles are applied to the surface in the presence of an atmosphere

containing oxygen and water vapour. Typically the particles are applied to the surface in the presence of air. However, the particles could be applied to the surface in the presence of an artificial atmosphere containing oxygen and water vapour.

Preferably, the zero valent metal particles are also exposed to water by applying the particles to the surface in admixture with water, or by applying water to the surface before, after or simultaneously with the application of the particles to the surface. The inventors have found that the rate of formation of hydroxyl radicals is greater the higher the concentration of oxygen in any water in contact with the particles. Thus when the particles are applied to the surface together with water so as to form a thin film of a mixture of the particles and water on the surface in the presence of air, the rate of formation of hydroxyl radicals in the thin film is greater than if the particles had been placed in a container of water exposed to air.

When the zero valent metal particles are applied to the surface and exposed to oxygen, for example from the surrounding atmosphere, the zero valent metal is rapidly oxidised by oxygen (in the case of zero valent iron, the Fe^0 is oxidised to form Fe(II)). The oxygen accepts electrons from the metal and forms a reduced form of oxygen (superoxide). In the presence of water, for example from the surrounding atmosphere, the superoxide self terminates to form hydrogen peroxide. The hydrogen peroxide reacts with the metal ion produced by the oxidation of the zero valent metal, to form highly oxidative hydroxyl radicals. These radicals are highly reactive and react with the contaminant, thereby oxidising the contaminant. In the case of toxic organic compounds such as halogenated organic compounds, chemical warfare agents and biological warfare agents, the product of the oxidation of the contaminant by the hydroxy radical is typically less harmful than the contaminant thus leading to the decontamination of the surface. Oxidation of the contaminant by the hydroxyl radical is the primary mechanism of chemically altering the contaminant in the method of the present invention. However, in some embodiments of the invention, the zero valent metal may itself also react with some of the contaminant reducing the contaminant, and the hydrogen peroxide may also react with some of the contaminant oxidising the contaminant.

Without wishing to be bound by theory, it is believed that for zero valent iron, the reactions resulting in the formation of the hydroxyl radicals are as set out below (where ">" represents adsorbed species):

$Fe^0 + O_2 \rightarrow\ >O_2$ (adsorption of oxygen onto iron particles)

$Fe^0 + >O_2 \rightarrow\ >Fe^{2+} + 2 >e^-$ (corrosion of iron)

$>O_2 + e^- \rightarrow\ >O_2^{\bullet-}$ (reaction of adsorbed O_2 with electrons)

$>Fe^{2+} \rightarrow Fe^{2+}$ (release of Fe^{2+} from iron particles into surrounding water)

$O_2^{\bullet-} + O_2^{\bullet-} + 2H^+ \rightarrow H_2O_2 + O_2$ (formation of hydrogen peroxide – this reaction may occur between adsorbed or released superoxide)

$Fe^{2+} + H_2O_2 \rightarrow FeOH^{2+} + OH^\bullet$ (Fenton reaction)

A similar Fenton-like reaction occurs between other metal ions such as Cu^+ and hydrogen peroxide to form hydroxyl radicals.

The zero valent metal particles may be any particles of a zero valent metal. Preferably the particles are nano-sized particles. Such particles are preferred as the larger surface area of the particles per unit weight compared to particles having a larger particle size, results in a more rapid oxidation of the metal and thus formation of hydroxyl radicals.

Preferably, the average primary particle size of the nano-sized zero valent metal particles is in the range of 0.5 to 3000 nm, more preferably 5 to 2000 nm, more preferably 10 to 1500 nm, more preferably 10 to 500 nm and more preferably 10 to 200 nm.

Nano-sized zero valent iron particles are typically in the form of an aggregate of the primary particles. Typically, the average aggregate (secondary) particle size is in the range of 0.1 to 10 µm, more preferably, 0.2 to 5 µm, more preferably 0.3 to 3 µm, and more preferably 0.5 to 2 µm.

Nano-sized zero valent metal particles may be prepared by methods known in the art. For example, nano-sized zero valent iron particles may be synthesised by reduction of an aqueous solution of Fe^{2+} or Fe^{3+} using a strong reducing agent such as sodium borohydride. This produces nano-sized zero valent iron particles having a primary

particle size of 1-200 nm. Similarly, nano-sized zero valent copper particles may be synthesised by reduction of an aqueous solution of Cu^{2+} using a strong reducing agent such as sodium borohydrate.

The zero valent metal particles may be applied to the surface by any means. Nano-sized zero valent metal particles may be applied to the surface as a dry powder. However, preferably, the nano-sized zero valent metal particles are applied to the surface in admixture with water, e.g. as a colloidal suspension in water.

When the zero valent metal particles are nano-sized particles, the particles are typically applied to the surface by spraying the particles on to the surface. Because of the size of such particles, a dispersion of the nano-sized zero valent metal particles in water can typically be sprayed on to the surface using conventional equipment used for spraying aqueous formulations on to a surface.

Prior to use in the method of the present invention, the zero valent metal particles can conveniently be stored as a mixture with water in the absence of oxygen or any other species that can oxidise the zero valent metal. Such a mixture may for example contain 10g to 100g of the zero valent metal particles per litre. In this form, the zero valent metal particles are non-toxic, non-flammable, non-corrosive and non-hazardous. When used to treat a contaminated surface, this mixture can be applied to the surface without modification using equipment, such as the Titan "Spraysafe" equipment, conventionally used to apply aqueous formulations to a surface.

The surface may be the surface of any solid substrate. The substrate may for example be a building, part of a building, furniture, machinery, vehicles such as motor vehicles, tanks or aircraft, or terrain such as a road, pathway or soil. The substrate may for example be personal equipment such clothing, protective clothing, protective glasses, helmets, hats etc. The substrate may for example be made of wood, glass, metal (e.g. steel, aluminium, etc), plastic, a fabric, or may be a painted surface. Preferably the substrate is formed of a material that is less reactive with hydroxyl radicals than the contaminant.

The contaminant may be any substance that has come to be in contact with the surface and that is capable of being oxidised by hydroxyl radicals. The contaminant may be an organic contaminant or an inorganic contaminant (e.g. arsenic (III) which can be oxidised to arsenic (V)). Typically, the contaminant is an organic contaminant. The

contaminant may for example be a toxic industrial pollutant such as a halogenated organic compound (e.g. a chlorinated aliphatic, chlorinated aromatic and/or polychlorinated biphenyl), a pesticide or herbicide. The contaminant may be a chemical or biological warfare agent. The chemical warfare agent may for example be one of the vesicant class of agents, such as sulphur mustard, nitrogen mustard and lewisite, or a nerve agent such as Tabun, Sarin, Soman or VX. The contaminant may be a toxin produced by biological organisms, such as the plant toxin ricin. The contaminant may also be a microorganism such as the potential biological warfare agents anthrax, Q-fever or Venezuelan equine encephalitis.

When toxic organic contaminants such as halogenated organic compounds, pesticides, herbicides, or chemical warfare agents are oxidised by the hydroxyl radicals, the oxidation product is typically harmless or less harmful to humans, animals and the environment than the organic contaminant. Depending on the intended use of the substrate and the toxicity of the oxidation products, the oxidation products may be allowed to remain on the surface, may be removed from the surface (e.g. by washing the surface or adsorption by an agent such as Fullers earth or charcoal) or the surface may be further treated to chemically alter the oxidation products.

The method of the present invention can be used to treat surfaces contaminated with a variety of contaminants. The method of the present invention can be carried out in the presence of air, and therefore can be used to treat surfaces of large fixed structures such as buildings, or terrain such as roads. As the method can be carried out in the presence of air, the method can be used to treat surfaces without requiring a specialised environment for the treatment process, and therefore can be used to treat the surfaces of equipment, clothing etc in the field.

The method advantageously does not require light or an external energy source to initiate the reactions leading to the chemical alteration of the contaminant. The method also advantageously does not require the presence of a strong metal binding ligand. Accordingly, in various embodiments of the invention, the zero valent metal particles are applied to the surface and exposed to oxygen and water without the presence of a strong metal binding ligand, such as EDTA.

In preferred embodiments, the zero valent metal particles are nano-sized zero valent iron particles. The nano-sized zero valent iron particles and the produced hydroxyl radicals can penetrate into the surface of porous substrates, and the hydroxyl radicals

are therefore able to react with contaminants adsorbed onto the surface and absorbed into the surface. The large surface area of nano-sized zero valent iron particles allows for a rapid oxidation of the iron resulting in rapid formation of hydroxyl radicals and therefore oxidation of the contaminants. A further advantage of the method of the present invention using nano-sized zero valent iron particles is that the ultimate oxidation product of the zero valent iron particles is nano-sized ferrihydrate particles. These particles have a large surface area and are capable of adsorption and hydrolysis of by-products of the oxidation of the contaminants.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method for treating a surface of a solid substrate to chemically alter contaminants on the surface capable of being oxidised by hydroxyl radicals, the method comprising applying to the surface particles of a zero valent metal capable of reacting with oxygen and water to form hydroxyl radicals, and exposing the particles to oxygen and water to form hydroxyl radicals at or near the surface.

2. A method according to claim 1, wherein the zero valent metal particles are exposed to oxygen and water by applying the zero valent metal particles to the surface in the presence of air.

3. A method according to claim 1 or 2, wherein the zero valent metal particles are applied to the surface in admixture with water.

4. A method according to any one of claims 1 to 3, wherein the zero valent metal is iron or copper.

5. A method according to any one of claims 1 to 4, wherein the zero valent metal particles are nano-sized zero valent metal particles.

6. A method according to claim 5, wherein the zero valent metal particles have a primary particle size in the range of 0.5 to 3000 nm.

7. A method according to claim 5 or 6, wherein the nano-sized zero valent metal particles are applied to the surface in admixture with water, and the mixture of the particles and water is sprayed onto the surface to form a film of the mixture on the surface.

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